



Synergetic effect of plasma/catalysis hybrid system for CH₄ removal

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ABSTRACT

Methane abatement from rich gas mixture was performed in a plasma-catalyst reactor. The inlet concentration of CH₄ varied from 0.15 to 1 vol.% of the total flow rate. Influences of different parameters such as temperature, gas composition and catalyst were investigated. The catalyst was an alumina wash-coated monolith made of cordierite containing 0.15 wt% of palladium and 15 wt% of Al₂O₃. The plasma was generated by means of a high voltage monopolar excitation. The higher the energy density, the higher the methane conversion. For plasma experiments carried out without catalyst, the CH₄ conversion reached a maximum of 33% for 1 vol.% CH₄ and 49% for 0.3 vol.% CH₄ in a N₂/O₂/CO₂/H₂O gas mixture (75/18.7/4/2 vol.%) at 200 °C and 1823 J L⁻¹. Carbon monoxide (CO) was observed to be the main product. The CO yield reached 29% and 49% for 1 and 0.3 vol.% CH₄, respectively. Moreover, experiments performed with a hybrid plasma-catalytic reactor showed two different behaviours depending on the catalyst location. In POST-plasma position, the presence of the catalyst did not modify the methane conversion but oxidized CO into CO₂. In IN-plasma position, the catalyst inhibited the methane conversion by decreasing the plasma volume between electrodes but oxidized CO into CO₂.

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1. Introduction

Many investigations have been performed for methane oxidation at low temperature by conventional heterogeneous catalysis and more recently by hybrid plasma-catalysis system. However, general applications of plasma using catalyst remain the conversion of methane into higher hydrocarbons (alkanes, alkenes, oxygenates) [1–4]. The use of a non-thermal plasma allows to generate a partly ionized gas containing highly reactive species such as highly energetic electrons, radicals, ionic and excited species, without heating the gas [5,6]. Recent investigations on methane oxidation assisted by non-thermal plasma (NTP) have been shown that C₂ hydrocarbons were the main products of conversion for methane with Ar as carrier gas. The presence of quartz in the plasma improved the methane (CH₄) conversion [7]. Mixtures of methane with oxygen (O₂) containing water (H₂O) and/or carbon dioxide (CO₂) were used for methane oxidation. Water and carbon monoxide were the main products for the reaction with oxygen. Heintze et al. showed that the carbon monoxide (CO) oxidation into carbon dioxide was favoured when Ni/α-Al₂O₃ catalyst was located in the plasma zone [8]. For a temperature lower than 200 °C [9],

the methane conversion was only due to plasma; the catalyst did not influence the yield and the selectivity; whereas for temperature higher than 200 °C the catalyst favoured the conversion of CO into CO₂. Steam reforming of methane has been investigated by Le et al. [10] by plasma technique without catalyst. The reaction products were C₂, C₃, hydrogen (H₂), CO, CO₂ and three kinds of coke were observed, (i) powder, (ii) soft coat and (iii) carbon filaments. Three types of catalysts have been used by Zhang et al. for methane dry reforming by NTP [11]: La₂O₃/γ-Al₂O₃, Pd/γ-Al₂O₃ and Pd-La₂O₃/γ-Al₂O₃. For all the catalysts, the methane conversion increased with the initial CO₂ concentration, whereas the selectivity towards C₂ compounds (acetylene C₂H₂, ethylene C₂H₄ and ethane C₂H₆) decreased. Recently, the activation of CH₄ and CO₂ to produce hydrocarbons has been studied by Pham et al. [4]. An excess of CH₄ (CH₄/CO₂ = 14) favoured the production of C₂ hydrocarbons while the formation of CO was limited. The use of the La₂O₃/γ-Al₂O₃ catalyst in the plasma zone, at 400 °C, increased significantly the activation of CO₂, leading to a higher CO selectivity, while it did not affect the activation of CH₄ and the CH₄ conversion remained stable. Jiang et al. [12] have showed that an A-zeolite with small pore size was more selective towards light hydrocarbons (C₂ and C₄) and inhibited the carbon black production and carbon polymerised films. For Pietruszka et al. [13], a gas mixture of O₂ and H₂O had a significant effect on the Ni/α-Al₂O₃ catalyst activation at low temperature. This effect might be due to water adsorption below 300 °C. Ayrault et al. [14] have observed that the presence of water

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in the gas phase induced a drastic decrease of ozone formation. However, only few investigations have been already published on plasma and monolith coupling for methane abatement in a complex gas mixture ($\text{CH}_4/\text{N}_2/\text{O}_2/\text{CO}_2/\text{H}_2\text{O}$). Pietruszka et al. studied the effect of the ($\text{CH}_4/\text{O}_2/\text{H}_2\text{O}$) gas mixture on plasma properties [13,15] whereas R. Marques et al. and J.L. Hueso et al. investigated the influence of the ($\text{CH}_4/\text{O}_2/\text{CO}_2/\text{NO}$) gas composition [16,17].

The present paper addresses catalytic combustion of methane in a plasma-catalyst hybrid system. Such system could be used in applications where the gas temperature is too low for catalytic oxidation of methane (automotive exhaust gas, unconverted methane in gas turbine, etc.). A $\text{Pd}/\text{Al}_2\text{O}_3/\text{cordierite}$ catalyst has been prepared and tested. Influence of different parameters, (i) gas composition, (ii) temperature and (iii) plasma power input has been studied with or without catalyst. The location of the catalyst within or forward the plasma zone was also investigated.

2. Experimental

2.1. Catalyst preparation

The catalyst used in this study was an alumina 15 wt% wash-coated monolith of cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) supplied by CTI (Céramiques Techniques Industrielles). The wash-coated monolith was impregnated with a solution of $\text{Pd}(\text{NO}_3)_2$ and dried at 60°C for 10 h. The fresh catalyst containing 0.15 wt% of palladium was calcined under air at 600°C for 4 h. For POST-plasma study, the honeycomb cylinder ($L=25.5$ mm, $\varnothing=12.7$ mm) was cut from a 400 cpsi type cordierite monolith. For IN-plasma experiment, the honeycomb was crushed and the biggest pieces were introduced in the electrode gap of the reactor between the dielectric and the inner electrode. Even in this configuration, the pressure drop remained low.

2.2. Plasma system

The non-thermal plasma was generated by means of a dielectric barrier discharge (DBD). The dielectric barrier was formed by a 1.8 mm thick glass tube with an outer diameter of 20 mm. The inner electrode was a 12 mm diameter stainless steel rod. The outer electrode (50 mm length) was made of Cu and wrapped around the glass tube. Both electrodes were connected to a high voltage monopolar pulse generator (40 kV, 1.5 kW, A2E Technologies-Enertronic) where the outer electrode was grounded. According to the size of the electrodes and the thickness of the dielectric, the volume of the plasma zone was about 0.79 mL. The time evolution of the discharge electrical parameters was measured by using a high-impedance probe for the applied voltage (Tektronix P6015A, 75 MHz) and by an inductive probe for the current (Stangenes Industries, 60 MHz), connected to a fast digital oscilloscope (Lecroy LT345, 500 MHz, 500 MS s^{-1}).

2.3. Reactant gas flow mixture preparation and analytical system

The gas composition was controlled by mass flow controllers for CH_4 , CO_2 and synthetic air, used as gas balance ($\text{N}_2/\text{O}_2=80/20$), whereas water was introduced by mean of a saturator system. The CH_4 content was varied from 0.15 to 1 vol.%, whereas CO_2 and H_2O concentration, when they were added in the reactant gas mixture was maintained at 4 and 2 vol.%, respectively. The total flow rate mixture was fixed at 400 or 600 mL min^{-1} and was analysed on-line. The carbonaceous products were analysed by gas chromatography (Varian 3400) equipped with a methanizer and with a FID detector. Ozone was monitored by an UV ozone analyser (O_3 42M, Environnement SA). In order to evaluate the reproducibility of the results some experiments have been repeated few times in the

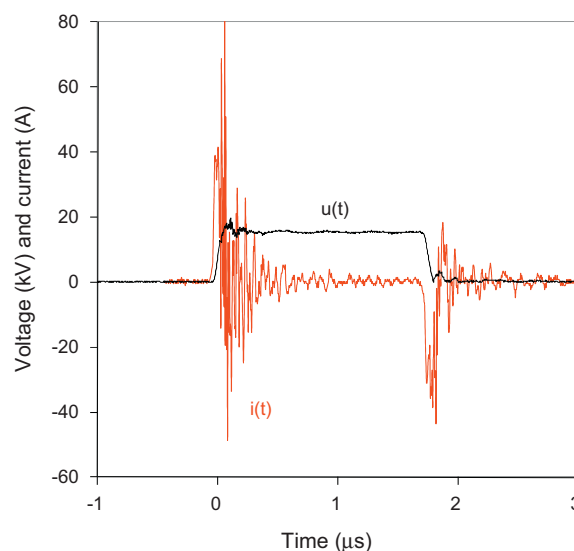


Fig. 1. Temporal evolution of the current during a voltage pulse ($U=15$ kV, $f=500$ Hz, total flow rate = 400 mL min^{-1} , GHSV = $30,400\text{ h}^{-1}$, $0.3\%\text{CH}_4/\text{N}_2/\text{O}_2/\text{CO}_2/\text{H}_2\text{O}$, Tr).

same conditions. The data precision concerning the CH_4 conversion rate and product yields is about $\pm 3\%$. However, the values given for the input energy were determined by mathematical calculation from the data obtained with the fast digital oscilloscope.

2.4. Experimental conditions

Space velocities of $30,400$ and $45,500\text{ h}^{-1}$ were obtained with a flow rate of 400 and 600 mL min^{-1} , respectively. Experiments were performed at room temperature (Tr) and at 200°C . The plasma generator supplied a voltage pulse at a constant voltage value equal to 15 kV. The input power was varied by modulating the frequency of the voltage pulse in the range of 100 – 500 Hz. Experiments were carried out without catalyst (plasma alone) and with catalyst positioned in POST-plasma or IN-plasma configurations.

3. Results and discussion

3.1. Plasma parameters

Ayrault et al. [14] have described the phenomena occurring during the time evolution of the current (evolution of voltage and current, charge and discharge of the equivalent capacitance). The plasma input energy was determined from the first part of the voltage pulse (increasing voltage) by integrating the voltage signal $u(t)$ and the current signal $i(t)$ monitored by the oscilloscope. An example of $u(t)$ and $i(t)$ signals is presented in Fig. 1. The voltage decreased at the end of the pulse generating a small current peak which was assumed to be due to the capacitance discharge of the plasma reactor without plasma formation. The input energy for a pulse was calculated by Eq. (1):

$$E(J) = \int_0^t u(t)i(t) dt, \quad (1)$$

with t being the pulse duration and the input energy density was determined by Eq. (2):

$$Ed \text{ (J L}^{-1}\text{)} = \frac{E(J)f(\text{Hz})}{Q(\text{L s}^{-1})}, \quad (2)$$

with f being the pulse frequency and Q being the flow rate. The current and the power (i.e. the energy density) deposited in the gas phase were directly proportional to the signal frequency. At

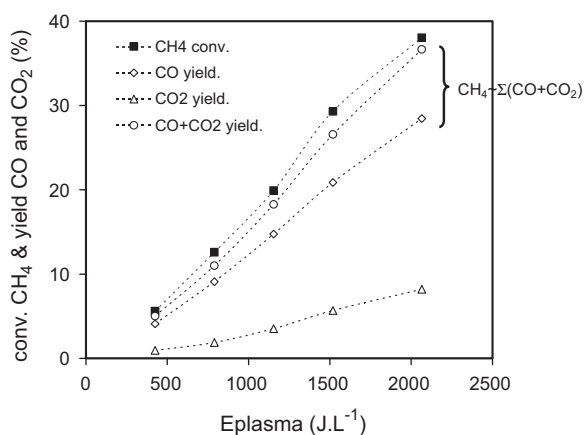


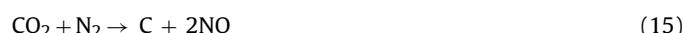
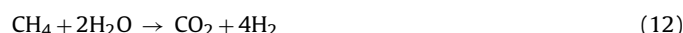
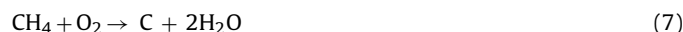
Fig. 2. Plasma alone: CH₄ conversion and CO and CO₂ yield as a function of the energy density (1%CH₄/N₂/O₂/H₂O, T=200 °C, 400 mL min⁻¹).

constant voltage of 15 kV and flow rate of 400 mL min⁻¹, the corresponding values of the current, power and energy density for a pulse frequency of 100 and 500 Hz are (0.6 A, 0.24 W, 365 J L⁻¹) and (3.0 A, 1.2 W, 1823 J L⁻¹), respectively. Hereafter are described the results of CH₄ abatement for plasma experiments carried out with and without catalyst.

3.2. Plasma effect without catalyst

This part deals with the results obtained for the oxidation of methane with plasma alone. Fig. 2 shows an example of CH₄ conversion and CO and CO₂ yields as a function of the input energy density. The conversion is proportional to the energy supplied and the carbon balance was complete since the amount of converted methane was close to the sum of CO and CO₂ formation. When CO₂ was introduced in the gas mixture, it was not possible to estimate the part of CH₄ oxidized into CO₂, and then the carbon balance, since the quantity of CO₂ formed by the methane conversion was negligible compared to the CO₂ introduced in the gas mixture (4 vol.%). Fig. 3 presents the CH₄ conversion rate and CO and CO₂ yields for various gas compositions (N₂/O₂, N₂/O₂ + CO₂, N₂/O₂ + H₂O and N₂/O₂ + CO₂/H₂O) at room temperature and 200 °C. At room temperature, the presence of CO₂ seemed to partly inhibit the methane conversion, whereas the presence of water (with or without CO₂) increased the methane conversion. The important CO yield (higher than methane conversion when CO₂ was added to the gas mixture) could be due to different reactions which could occur under

these plasma conditions: (i) methane oxidation by O₂ thanks to oxygen species generated in the plasma (O•, OH•) (Eqs. (3)–(7)), (ii) methane dry reforming [18] (Eqs. (8) and (9)) and (iii) methane steam reforming (Eqs. (10)–(12)). Moreover, chromatographic analysis with a 5A molecular sieve did not reveal the presence of hydrogen (H₂) peak but two others peaks appeared. It was assumed that both peaks were attributed to NO and NO₂ formation. In addition, for experiments with CO₂ in the inlet gas mixture, C powder was deposited on the inner electrode. The mechanisms for nitrogen monoxide (NO) and nitrogen dioxide (NO₂) production and C deposition are presented in Eqs. (13)–(16).



Concerning the ozone formation, Fig. 4 shows the decrease of O₃ concentration as a function of power. Either the ozone was consumed during the reaction or ozone production decreased with increasing the power or combination of both processes. A study carried out by Ayrault et al. [14] showed that the ozone production was decreasing with increasing the power. The authors suggested that such fast ozone consumption was due the presence of steam. Moreover, an increase of the plasma energy could elevate the gas temperature, leading to the thermal decomposition of O₃.

Finally, at constant input energy density the methane conversion increased when its initial concentration decreased as shown in Fig. 5, which suggests that the kinetic order is close to zero. Table 1 summarises the best performances obtained with plasma alone for methane conversion and CO yield. For a constant energy density

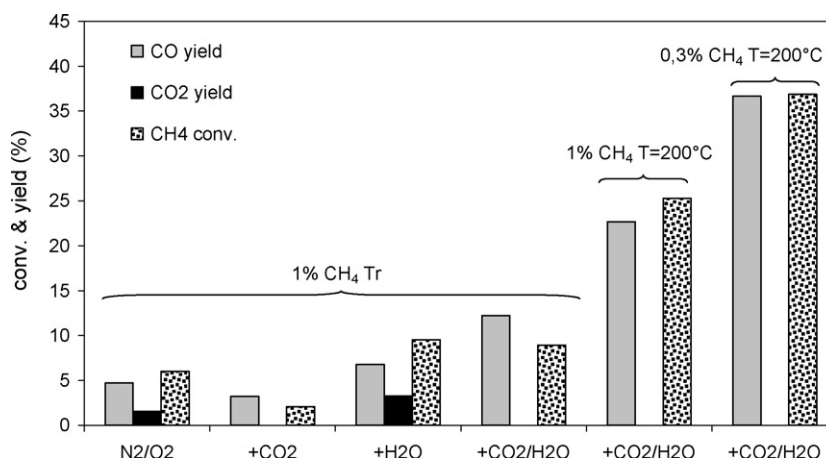


Fig. 3. CH₄ conversion and CO and CO₂ yield as function of gas composition and temperature (P=9.7 W, E=1 458 J L⁻¹, 400 mL min⁻¹).

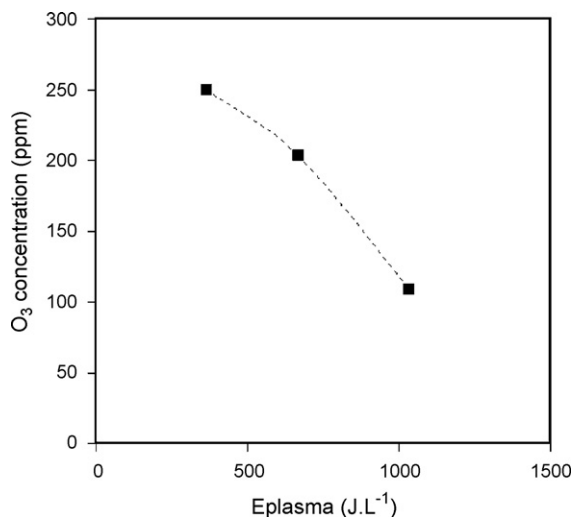


Fig. 4. Evolution of the ozone concentration (1%CH₄/N₂/O₂/CO₂/H₂O, Tr, 400 mL.mn⁻¹).

Table 1
Maximum of CH₄ conversion and CO production for the study with plasma alone (T = 200 °C, P = 12.2 W, N₂/O₂/CO₂/H₂O).

%CH ₄	Flow rate (mL min ⁻¹)	E _{plasma} (J L ⁻¹)	CH ₄ conv. (%)	CO yield (%)
1	400	~1823	33	29
0.3	400		49	45
0.3	600		37	32
0.15	600		38	48

of 1823 J L⁻¹, the highest CH₄ conversion rate (49%) was obtained with an initial methane concentration of 0.3 vol.% and a flow rate of 400 mL min⁻¹. However, in these conditions, the CO yield reached 45%.

3.3. Plasma effect with catalyst

The catalyst was introduced in the reactor as an alumina-washcoated cordierite monolith (see Section 2.1).

The experimental conditions used a gas mixture composed of CH₄ varying from 0.3 to 1 vol.% and O₂/N₂/CO₂/H₂O (air ratio balance/4/2) at a temperature of 200 °C. Two possibilities of catalyst location have been investigated, (i) in the plasma zone and (ii) downstream to the plasma zone. The results were compared with

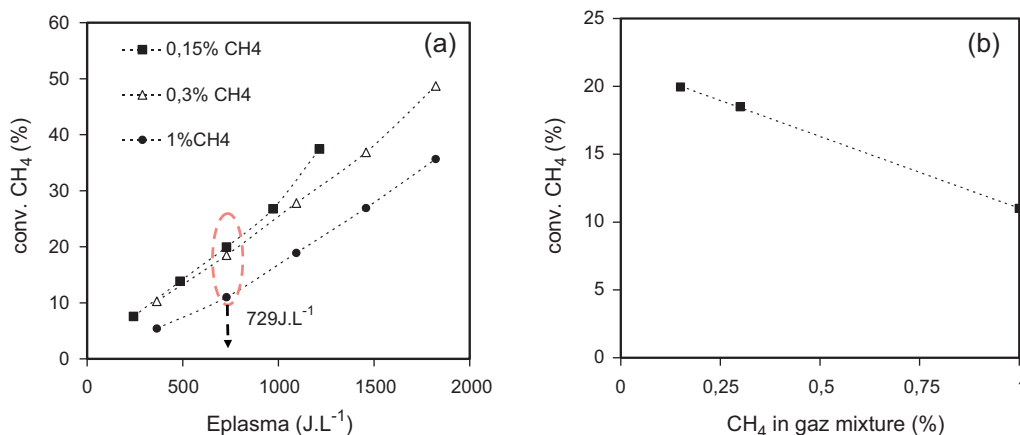


Fig. 5. CH₄ conversion versus input energy and methane concentration in the inlet gas mixture (a) and at P = 729 J L⁻¹ (b).

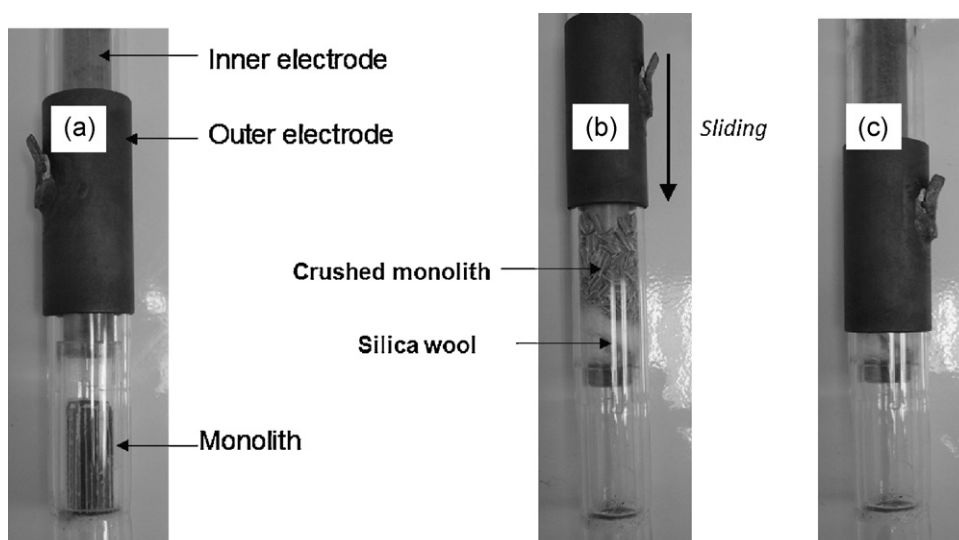


Fig. 6. Monolith in POST-plasma (a) and IN-plasma configuration showing the crushed monolith with the outer electrode shifted to the top of the reactor (b), working position (c). As dimension scale, the inner electrode diameter is 12 mm.

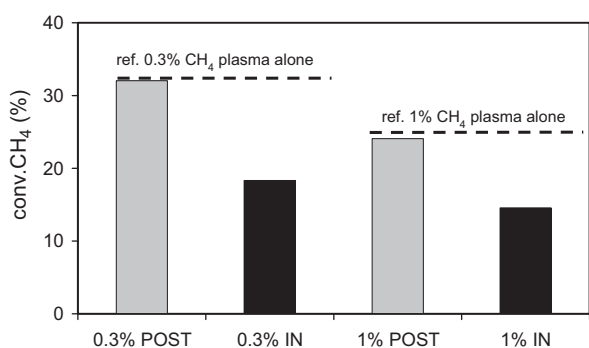


Fig. 7. CH₄ conversion for POST and IN-plasma configuration and reference ($x\text{CH}_4/\text{N}_2/\text{O}_2/\text{CO}_2/\text{H}_2\text{O}$, x being the inlet CH₄ concentration 0.3 or 1 vol.%; $T=200^\circ\text{C}$; $P=9.7\text{ W}$; $E_p=1458\text{ J L}^{-1}$; 400 mL min^{-1} ; dotted line: plasma alone).

those obtained with the plasma alone. For the IN-plasma catalyst location, the monolith was crushed in order to place the catalyst in the annular zone between the inner electrode and the reactor wall. Fig. 6 shows the catalyst location for both cases, POST and IN-plasma, while methane conversion is plotted in Fig. 7. The reference was the methane conversion for experiments carried out with plasma alone. Whatever its location, the catalyst did not improve the methane conversion. When the catalyst was located IN-plasma, the methane conversion was almost divided by two. The main result concerned the CO formation which was totally suppressed by the catalyst, whatever its location. The simplest configuration with the catalyst in POST-plasma location allowed to reach the same performances than the plasma alone but without any CO formation.

So as to better understand the role of the catalyst in the plasma zone, two experiments have been carried out. As presented in Fig. 8, either (i) the catalyst could hold only the upper half of the plasma zone length (upstream catalyst, configuration 1), or (ii) the catalyst could hold only the lower half of the plasma zone length (downstream catalyst, configuration 2). These both configurations involved that a pure plasma zone was present after or before the catalyst. Whatever the catalyst location in the plasma zone and whatever the initial methane concentration (0.3 and 1 vol.%), the methane conversion remained the same as shown in Fig. 9. Moreover, as previously observed with the plasma alone (without catalyst), in the case where the catalyst was in the upstream position, the methane conversion led to the formation of CO. The catalyst downstream position increased the CO₂ selectivity by oxidizing the CO into

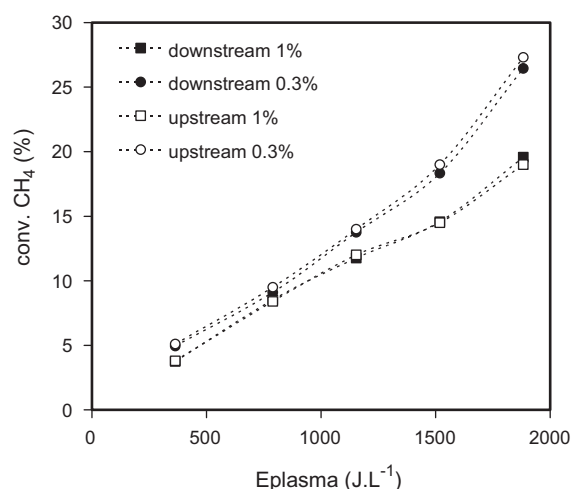


Fig. 9. CH₄ conversion for catalyst IN-plasma (downstream and upstream positions) ($\text{CH}_4/\text{N}_2/\text{O}_2/\text{CO}_2/\text{H}_2\text{O}$, $T=200^\circ\text{C}$, 400 mL min^{-1}).

Table 2

Maximum CH₄ conversion for POST or IN-plasma position ($T=200^\circ\text{C}$, $P=12.2\text{ W}$, $\text{N}_2/\text{O}_2/\text{CO}_2/\text{H}_2\text{O}$, 400 mL min^{-1}).

Catalyst position	%CH ₄	E_{plasma} (J L ⁻¹)	CH ₄ conv. (%)
POST-plasma	1	~1823	33
	0.3		44
IN-plasma	1		20
	0.3		27

CO₂, as evidenced when the catalyst was in POST-plasma position, where CO was not detected. The presence of a solid in the electrode gap in the plasma reactor seemed to limit the plasma zone to the part of the reactor without the crushed monolith. Moreover, the residence time of the gas mixture in the reactor reactive zone was decreased, leading to a decrease in the methane conversion.

To summarize, the best performances obtained for each configuration at constant input energy are presented in Table 2. For a constant energy density of 1458 J L^{-1} , the highest CH₄ conversion rate (32%) was obtained with an initial methane concentration of 0.3 vol.% and a flow rate of 400 mL min^{-1} without CO production.

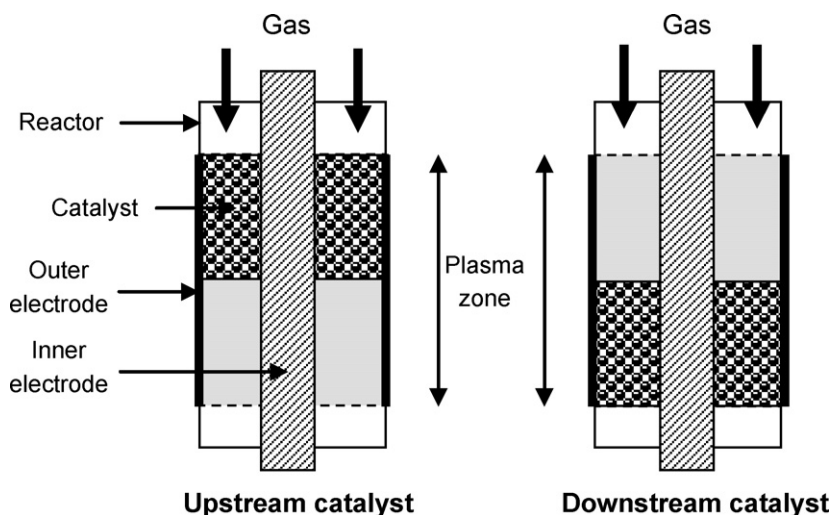


Fig. 8. Catalyst in upstream or downstream configurations.

The POST-plasma configuration was observed to be the optimal conditions for the plasma-catalyst reactor. From design point of view, the implementation of this configuration is simple compared with the one where the catalyst has to be introduced in the plasma zone.

4. Conclusion

Methane abatement has been performed by a DBD plasma/catalysis hybrid system. A Pd-based monolith was used as catalyst. Different parameters have been investigated, (i) gas composition (CH_4 , N_2 , O_2 , CO_2 , H_2O), (ii) temperature (T_r and 200°C), (iii) methane concentration (0.15, 0.3 and 1 vol%) and (iv) plasma/catalyst configuration (catalyst POST or IN-plasma). The main conclusions are:

- (1) In the absence of catalyst (plasma alone), the presence of CO_2 in the gas mixture inhibited partly the methane conversion, whereas the presence of steam balanced this inhibiting effect but increased the CO formation. The CH_4 conversion increased when the temperature in the plasma zone and the energy density increased and when the initial CH_4 concentration decreased.
- (2) In the presence of catalyst, no synergy effect between plasma and catalyst was observed. Moreover, CH_4 conversion decreased when the catalyst was located in the plasma zone due to the decrease of the residence time of the reactant in the reactive zone. Whatever the catalyst location (POST- or IN-plasma), the effect of the catalyst was only to achieve complete CO oxidation into CO_2 .
- (3) The best configuration proposed was the use of pure DBD reactor followed by an oxidation catalyst, allowing also to simplify the reactor design.

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